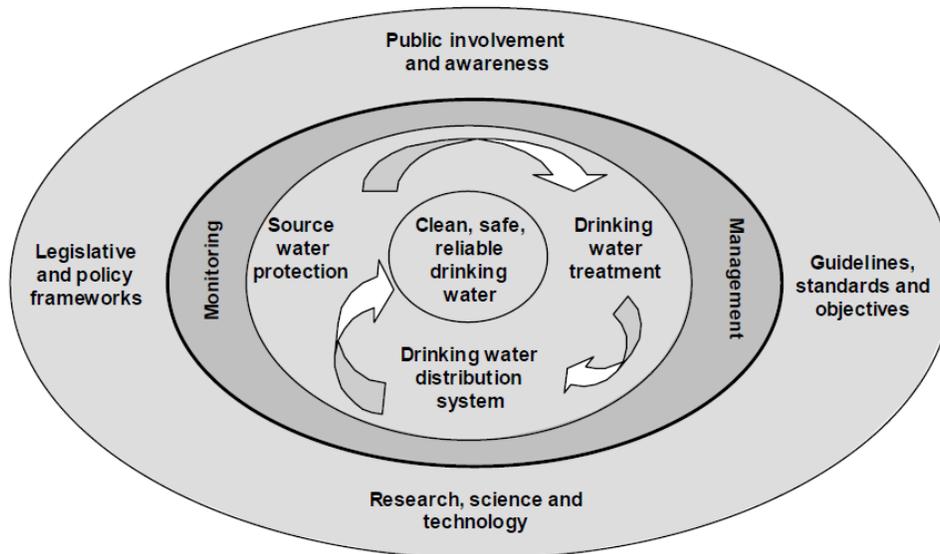


Figure 1. Multi-Barrier Approach



Source: Canadian Council of Ministers of the Environment (2002). *From Source to Tap*.

Rice pesticides are of interest to Sacramento River drinking water utilities because over the last two decades, on many occasions pesticides used only on rice have been detected at drinking water treatment plant intakes. The efforts of the rice industry and regulatory agencies through the Rice Pesticide Program have resulted in significant reductions in frequency and detected levels of thiobencarb in the Sacramento River. However, the historic presence of rice pesticides at plant intakes demonstrates that there are pathways for water pollutants in rice discharges to reach downstream water supplies.

For pesticides, source water protection efforts are focused on working within the existing regulatory and management programs that manage the various potential contaminating activities, such as the California Department of Pesticide Regulation (DPR), the Central Valley Regional Water Quality Control Board (Water Board), and the U.S. EPA Office of Pesticide Programs.

Drinking Water Standards

There are numerous pesticides currently regulated in treated drinking water either by the U.S. EPA or by the DPH (see <http://water.epa.gov/drink/contaminants/index.cfm> and <http://www.cdph.ca.gov/certlic/drinkingwater/Pages/default.aspx>). Note that California has its own drinking water standards for some constituents and that in California, both primary and secondary Maximum Contaminant Levels are enforceable.

In addition to drinking water standards, DPH has developed Notification Levels for additional constituents of interest (DPH 2012). These are health based levels that require action by the water utility, ranging from public notification to treatment, if found above the Notification Levels. Similar action is required for a related set of values known as “archived advisory levels” (DPH 2012).

U.S. EPA has also developed Health Advisories for other constituents in drinking water that are not currently regulated. These are non-enforceable levels which can provide guidance to water systems on the potential risk to public health. The Health Advisories include acute and chronic risk for cancer and non-cancer health effects. U.S. EPA has conveniently compiled Federal drinking water standards, including health advisories, into a reference handbook (U.S. EPA 2012a).

Drinking water standards are not static. The U.S. EPA Office of Groundwater and Drinking Water has several programs in place to review the current drinking water standards (called the Six Year Review) as well as identify new constituents which may require a new drinking water standard (the Contaminant Candidate List). Another USEPA program that may affect drinking water standards is the Endocrine Disrupters Screening Program, which is evaluating chemicals for potential non-cancer impacts to the endocrine system. This program could potentially lead to new or revised primary drinking water standards if they are determined to be of human health concern.

Drinking Water Benchmarks

For those pesticides without drinking water standards, U.S. EPA has developed Human Health Benchmarks for use by the states in water quality management. These values, which are periodically updated, are available on the Internet (U.S. EPA 2012b).

Pesticide Prioritization Methodology

The SRSWPP pesticide prioritization methodology, known as the Risk Screening Ratio method, involves the following steps:

1. Obtain Sacramento River watershed pesticide use data from DPR (DPR 2013a). (The most recent data currently available are from calendar year 2011).
2. Obtain human health impact reference values for each pesticide. Use standards where available (U.S. EPA 2012a; DPH 2012); otherwise, use U.S. EPA Human Health Benchmarks (U.S. EPA 2012b). (Care must be taken in selection of these values, as available benchmark values are often not comparable because they are based on varying levels of acceptable human health risk, and newer values may reflect important new scientific information.)
3. Calculate the ratio of quantity of each pesticide used, by sector, to the human health impact benchmark values. Rank these "Risk Screening Ratios" from largest to smallest.
4. For those pesticides with the highest Risk Screening Ratios, review other available information about the pesticide, such as the pesticide's environmental fate, available water quality monitoring data, and U.S. EPA modeling results to determine if available information is sufficient to establish a final priority level. Water quality monitoring data can provide the most valuable input and can come from watershed-wide monitoring programs, scientific researchers, government agencies like USGS, the Water Board, water utilities, and DPR, and participants in regulatory programs like the Water Board Irrigated Lands Regulatory Program. It is important to verify the data quality, the detection limits (which may be higher than benchmarks), and that the data was collected in a manner and timeframe consistent with pesticide use patterns.

Rice Pesticide Prioritization 2013

Table 1 presents a summary of the 25 pesticides most heavily used (on the basis of the quantity of pesticide active ingredient) used on rice in 2011. Table 1 provides the selected human health drinking water reference values for 24 of these pesticides (no value is currently available for limonene). A risk ratio has been calculated for each pesticide with a reference value. The table is sorted by the risk ratio to provide the initial prioritization list.

Table 2 presents the second portion of the review, which brings in available scientific information (primarily water quality monitoring data) for the ten highest ranked pesticides. On the basis of this information, Table 2 includes recommendations for potential next steps for consideration by the SRSWPP. The key recommendations (see highlighted rows in the table) are to request monitoring of propanil and its major degradate 3,4-dichloroaniline, and chlorate in the Rice Waste Discharge Requirements under the Water Board Irrigated Lands Regulatory Program. Periodic copper monitoring should also be considered under the Rice Waste Discharge Requirements to confirm that future management practices continue to keep copper concentrations below regulated levels.

The propanil degradate 3,4-dichloroaniline is a new addition to this list. There are outstanding questions about the health implications of this degradate, which have been raised by the Water Board and others (primarily in relationship to a proposed Basin Plan Amendment for Diuron, which also degrades to 3,4-dichloroaniline). New scientific data just collected this year by the USGS identified a strong linkage between 3,4-dichloroaniline and propanil (Orlando and Hladik 2013). Previously, it had been thought to primarily occur in the Sacramento/San Joaquin River watershed as a consequence of diuron degradation.

Pesticide priorities have changed with each of the three rice pesticide prioritizations conducted for the SRSWPP. Changes occurred in response to changes in pesticide use, new monitoring data, and new scientific information about pesticide hazards. Recognizing that regulatory actions like U.S. EPA's 15-year cycle of Registration Reviews, new pesticide products, and a backlog of U.S. EPA and U.S. Fish and Wildlife Service pesticide "consultations" under the Endangered Species Act will continue to have significant effects on Sacramento Valley pesticide usage, the source water protection program will have best information if it updates this prioritization every 2-3 years.

Table 1. Initial Rice Pesticide Prioritization

Pesticide	2011 Use (lb. a.i.)	Drinking Water Reference Value (µg/L)	Type of Reference Value	2011 Risk Ratio *	Priority Ranking
Thiobencarb	246,927	1	Enforceable Secondary DWS	246,927	1
Propanil**	2,221,673	63	HHBP - Chronic	35,265	2
Copper Sulfate (Pentahydrate)	1,069,824	1,000 (Copper)	Enforceable Secondary DWS	1,070	3
Lambda-Cyhalothrin	4,737	7	HHBP - Chronic	677	4
Cyhalofop Butyl	25,607	70	HHBP - Chronic	366	5
Sodium Chlorate	32,521	210	HHBP - Chronic	155	6
Triclopyr, Triethylamine Salt	63,845	350	HHBP - Chronic	182	7
Pendimethalin	4,776	210	HHBP - Chronic	23	8
2,4-D, Dimethylamine Salt	3,050	70 (2,4-D)	Enforceable Primary DWS	44	9
Azoxystrobin	46,083	1,260	HHBP - Chronic	37	10
Clomazone	132,786	5,880	HHBP - Chronic	23	11
Glyphosate (Isopropylamine Salt + Potassium Salt)	12,068	700	Enforceable Primary DWS	17	12
Mancozeb	9	0.6	HHBP – Cancer (10 ⁻⁶ risk)	15	13
Trifloxystrobin	2,921	266	HHBP - Chronic	11	14
Paraquat Dichloride	101	30	Health Advisory - Lifetime	3	15
Carfentrazone-Ethyl	722	210	HHBP - Chronic	3	16
Difluzenuron	244	140	HHBP - Chronic	2	17
Penoxsulam	4,817	1,029	HHBP - Chronic	5	18
Bispyribac-Sodium	2,574	700	HHBP - Chronic	4	19
Propiconazole	3,212	700	HHBP - Chronic	5	20
(S)-Cypermethrin	1,444	420	HHBP - Chronic	3	21
Bensulfuron Methyl	3,325	1,400	HHBP - Chronic	2	22
Orthosulfamuron	263	350	HHBP - Chronic	1	23
Carbaryl	804	700	Archived Advisory Level	1	24
Limonene	5,015	-	None available	?	25

Sources: DPR Pesticide Use Reporting Database (DPR 2013a). Total quantity of pesticide active ingredient (a.i.) applications reporting in 2011 as used on rice.

DWS = California or U.S. EPA established Drinking Water Standard. Note that all DWS are enforceable in California, including secondary standards.

HHBP = U.S. EPA Human Health Benchmark for Pesticides (U.S. EPA 2012b); Health Advisory (U.S. EPA 2012a); Notification Level (DPH 2012)

*Ratio of use quantity to drinking water benchmark.

**Does not include degradate 3,4-dichloroaniline; there are outstanding questions about the health implications of this degradate.

Table 2. Evaluation of Ten Highest Ranking Rice Pesticides

Pesticide	Drinking Water Benchmark (µg/L)	Evaluation	Recommendation
Thiobencarb	1	Managed through the RPP	Continue to manage through the RPP.
Propanil	63	Monitoring has been conducted by both CRC and USGS. Both propanil and a major degradate that is currently being investigated by the Water Board to answer questions about its human health and aquatic toxicity – 3,4-dichloroaniline (3,4-DCA) – have been detected in the watershed on more than 100 occasions at concentrations up to 47 µg/L (Hladik 2011; CRC 2011; DPR Surface Water Database 2013b). Recent monitoring by the USGS (Orlando and Hladik, 2013) showed that propanil degradation is the source of most 3,4-DCA in the watershed and that concentrations of the degradate were often three or more times the concentration of propanil.	Request monitoring of propanil and its major degradate 3,4-dichloroaniline in the Rice WDRs.
Copper Sulfate (Pentahydrate)	1,000 (Copper)	Multiple monitoring programs (e.g., USGS 2000) and water utility monitoring have sampled for copper, which is consistently detected at concentrations well below the benchmark in the Sacramento River.	A limited amount of confirmation monitoring may be appropriate to be addressed in the Rice WDRs. Enough monitoring data are available to demonstrate that current management practices provide sufficient protection for source water quality. Future monitoring may be appropriate to confirm that management practices at that time provide sufficient protections.
Lambda-Cyhalothrin	7	Detected in watershed monitoring, but at concentrations orders of magnitude lower than the human health benchmark (e.g., Weston 2010, CRC 2003-2006). Used on multiple types of crops in the watershed.	Water Board and DPR management measures for pyrethroids that are intended to protect aquatic life (including the upcoming pyrethroids Basin Plan Amendment), should provide sufficient protection for source water quality, since pyrethroids' aquatic toxicity occurs at concentrations 100-1,000 times lower than human health benchmarks for pyrethroids.

Table 2. Evaluation of Ten Highest Ranking Rice Pesticides (Continued)

Pesticide	Drinking Water Benchmark (µg/L)	Evaluation	Recommendation
Cyhalofop Butyl	70	Watershed monitoring by the CRC in 2008 and 2009 resulted in no detections, with a reporting limit of 0.1 µg/L (CRC 2008, 2009).	Consider monitoring again if usage grows or benchmark decreases.
Sodium Chlorate	210	Creates chlorate ion in water. We have not identified any readily available monitoring data for rice or for the watershed.	Continue to track regulatory developments on sodium chlorate. Consider requesting monitoring of chlorate in the Rice WDRs.
Triclopyr, Triethylamine Salt	350	Becomes triclopyr in water. CRC monitoring in 2008 and 2009 resulted in a peak detection of 0.71 µg/L. U.S. EPA reported that DPR has detected in the watershed at concentrations up to 14.5 µg/L (U.S. EPA 2009).	Consider monitoring again if usage grows or benchmark decreases.
Pendimethalin	210	CRC monitoring in 2008 and 2009 resulted in no detections, with a reporting limit of 0.2 µg/L (CRC 2008, 2009). USGS detected at nanograms per liter concentrations, which is orders of magnitude below benchmark (Hladik 2011).	Consider monitoring again if usage grows or benchmark decreases.
2,4-D, Dimethylamine Salt	70	Becomes 2,4-D in water. Used on many other crops in the watershed. Monitoring data from the 1990s, when use on rice was greater, showed concentrations consistently less than 3 µg/L in the Sacramento Valley's rice growing area (DPR Surface Water database 2013b).	Additional monitoring for rice is unnecessary from the source water protection perspective. Enough monitoring data are available to demonstrate that current management practices for rice provide sufficient protection for source water quality.
Azoxystrobin	1,260	CRC monitoring in 2008 and 2009 resulted in peak detection of 0.87 µg/L. Watershed monitoring by USGS in 2010 had frequent detections, majority <25 µg/L, but one was >120 µg/L benchmark (Hladik 2011). Recent USGS monitoring of the Sacramento River at Freeport found a maximum concentration of <0.4 µg/L (Orlando and Hladik 2013).	Consider monitoring again if usage grows or benchmark decreases.

References

- California Department of Pesticide Regulation (DPR) (2013a). Pesticide Use Reporting (PUR) Database. <http://www.cdpr.ca.gov/docs/pur/purmain.htm> Accessed August 2013.
- California Department of Pesticide Regulation (DPR) (2013b). Surface Water Database. <http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm> Accessed August 2013.
- California Department of Public Health (DPH) (2012). Drinking Water Notification Levels and Response Levels: An Overview. DPH Drinking Water Program. <http://www.cdph.ca.gov/certlic/drinkingwater/Pages/NotificationLevels.aspx>
- California Rice Commission (CRC) (2003-2006). Various monitoring reports submitted to the Central Valley Water Board.
- California Rice Commission (CRC) (2008). Conditional Waiver for Rice and Rice Pesticides Program. 2008 Annual Monitoring Report Sacramento River Drainage Basin.
- California Rice Commission (CRC) (2009). Conditional Waiver for Rice and Rice Pesticides Program. 2009 Annual Monitoring Report Sacramento River Drainage Basin.
- California Rice Commission (CRC) (2011). Conditional Waiver for Rice and Rice Pesticides Program. 2011 Annual Monitoring Report Sacramento River Drainage Basin.
- Hladik, M.; Smalling, K. L. et al., USGS California Water Science Center (2011). Pesticide Runoff from Sacramento Valley Rice Fields.” Presentation at NorCal SETAC. May 5. (Paper in preparation by K. Kuivila, M. Hladik et al.)
- Orlando, J. and Hladik, M. (2013). “Changes in Pesticide Use and Concentrations Entering the Sacramento/San Joaquin Delta: 1990's vs the Present.” Presentation at Delta Pelagic Organism Decline Contaminants Work Team Meeting, August 6.
- U.S. EPA (2009). Risks of Triclopyr Use to Federally Threatened California Red-legged Frog (*Rana aurora draytonii*). Pesticide Effects Determination. Prepared by the Office Pesticide Programs Environmental Fate and Effects Division.
- U.S. EPA (2012a). *Drinking Water Standards and Health Advisories Office of Water*. 2012 Edition. EPA 822-S-12-001. <http://water.epa.gov/action/advisories/drinking/upload/dwstandards2012.pdf>
- U.S. EPA (2012b). U.S. EPA Human Health Benchmarks for Pesticides. <http://www.epa.gov/pesticides/hhbp>
- USGS (2000). *Water-Quality Assessment of the Sacramento River Basin, California: Water-Quality, Sediment and Tissue Chemistry, and Biological Data, 1995-1998*. USGS Open-File Report 2000-391.
- Weston D. P. and M. J. Lydy (2010). "Urban and Agricultural Sources of Pyrethroid Insecticides to the Sacramento-San Joaquin Delta of California." *Environmental Science & Technology* **44**(5): 1833–1840.